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(57) Abrégé/Abstract:

Hydrocarbonaceous fuels and additive compositions therefor which comprise: a) one or more fuel-soluble manganese carbonyl compounds; b) one or more fuel-soluble alkali or alkaline earth metal-containing neutral or basic detergent salts; and c) one or more fuel-soluble metal deactivators of the chelation type. These compositions preferably contain, in addition to components a), b) and c) above, one or more of the following: d) at least one fuel-soluble ashless dispersant; e) at least one fuel-soluble demulsifying agent; and f) at least one aliphatic or cycloaliphatic amine. Component c) enhances the stability of fuel compositions containing at least components a) and b). The compositions possess improved combustion characteristics (e.g., formation of less soot, smoke, carbonaceous products and/or noxious emissions), and form on combustion carbonaceous products of reduced acidity. The deposition of sludge on critical engine or burner parts or surfaces is reduced and the fuels have improved demulsibility characteristics. And the fuel compositions can result in decreased fuel consumption in diesel engines.

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HYDROCARBONACEOUS FUEL COMPOSITIONS AND  
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This invention relates to liquid fuel compositions of enhanced properties, particularly as regards combustion and stability characteristics.

5 Heretofore certain organometallic compounds have been found effective as combustion improvers for distillate fuels such as home heating oils and the like. For example U.S. Pat. No. 3,112,789 describes the use of cyclopentadienyl manganese tricarbonyls for this purpose, and the compound methylcyclopentadienyl manganese tricarbonyl (MMT) has been sold in the form of a solution in a hydrocarbon diluent  
10 as a combustion improver for distillate fuels of this type. Bis(cyclopentadienyl) iron has also been promoted and sold as a combustion improver for use in such fuels.

15 Keszthelyi et al report in Period. Polytech. Chem. Eng., Volume 21(1), pages 79-93 (1977) that in the combustion of light fuel oils in evaporating burners, 0.025% cyclopentadienyl manganese tricarbonyl was effective for soot reduction. And in Margantsevye Antidetonatory, edited by A. N. Nesmeyanov, Nauka, Moscow, 1971, at pages 192-199, Makhov et al report test work indicating that addition of cyclopentadienyl manganese tricarbonyl to diesel fuel reduces the level of smokiness of the exhaust gases.

20 Zubarev et al in Rybn. Khoz. (Moscow), Volume 9, pages 52-4 (1977), report test results on the addition to a fuel mixture of diesel fuel and marine residual fuel of cyclopentadienyl manganese tricarbonyl (CMT) alone or in a blend containing "a scavenger and a solvent". It is indicated that the CMT alone reduced carbon deposits on the intake valves but not on other engine surfaces, and that it reduced smoke. The CMT blend ("Ts8") is reported to have reduced carbon deposition more effectively, especially on the intake valves, cylinder head and piston head.

25 Canadian Patent No. 1,188,891 describes an additive for fuel oils and diesel fuels and other liquid combustibles and motor fuels designed to improve combustion, reduce soot formation and enhance storage stability. Such additive is composed of at least one oil-soluble or oil-dispersible organic compound of a transition metal or 30 an alkaline earth metal; and at least one oxidation and polymerisation inhibitor for

hydrocarbons stable at temperatures of at least 300°C. According to the patentee, the presence in such fuels of compounds of transition metals such as copper, manganese, cobalt, nickel and iron accelerate fuel deterioration in accelerated stability tests conducted at 149°C in the presence of air. Such compounds as MMT,  
5 Ferrocene, copper naphthenate, iron naphthenate, and manganese naphthenate are indicated to cause such deterioration in the absence of a high temperature (e.g., 300°C) stabiliser such as heat-stable alkyl phenols, amines, aminophenols, dithiophosphates, dithiocarbamates and imidazoles and inorganic inhibitors in the form of oxides or hydroxides of aluminum, magnesium or silicon. EP 0078249 B1 is  
10 to the same general effect, and indicates that the additive may be a combination of a transition metal compound and an alkaline earth metal compound, as well as either such compound separately.

G.B. Patent No. 1,413,323 describes a multi-component diesel fuel additive to avoid or reduce the formation of deposits on injector parts. The additive comprises,  
15 inter alia, an ester of oleic or naphthenic acid having an acid number below 200; a naphthenic acid ester of cresol; an alkoxyalkyl ester of an aliphatic carboxylic acid; an organometallic tricarbonyl cyclopentadiene compound such as cyclopentadienyl manganese tricarbonyl; an amide derivative of a polyolefin obtained by the reaction  
20 of a polyolefin substituted succinic acid or anhydride with a polyamine; a copolymer of ethylene and a vinyl (or hydrocarbyl-substituted vinyl) ester of a carboxylic acid wherein the copolymer has a number average molecular weight of more than 3000; a re-odoriser composed of a mixture of natural and synthetic alcohols, ketones and ethers; kerosene; and a petroleum distillate.

U.S. Pat. No. 4,505,718 describes compositions comprising the combination of  
25 a transition metal salt such as a manganese carboxylate, and an ashless hydrocarbon-soluble ashless dispersant. An optimum balance between beneficial and deleterious effects is said to be achieved in oils of lubricating viscosity and hydrocarbon fuels.

Additive compositions based on or including one or more fuel-soluble manganese carbonyl compounds and one or more fuel-soluble alkali and/or alkaline earth metal-containing detergents have been found in these laboratories to provide  
30 excellent improvements in the combustion characteristics of various hydrocarbon-

aceous fuels. Unfortunately, in many cases such additive combinations can cause fuel destabilisation -- i.e., the additives can cause the hydrocarbonaceous fuel with which they are blended to be less stable on exposure to air or oxygen at elevated temperatures than the fuel would be absent such additives.

5 Thus a need has arisen for an effective way of preventing such fuel destabilisation without interfering with the combustion-enhancing effectiveness of such additive combinations and without materially increasing the cost of the additive combinations. This invention is deemed to fulfill this need in a most efficacious manner.

10 In accordance with this invention destabilisation of liquid hydrocarbonaceous fuels containing a combination of at least one fuel-soluble manganese carbonyl compound and at least one fuel-soluble alkali or alkaline earth metal-containing detergent is inhibited by inclusion in the fuel of at least one fuel-soluble metal deactivator of the chelation type, i.e., a metal deactivator capable of complexing dissolved metals or metal ions.

15 Thus in one of its embodiments this invention provides an additive composition for hydrocarbonaceous fuels. Such additive composition comprises:

- a) one or more fuel-soluble manganese carbonyl compounds;
- b) one or more fuel-soluble alkali or alkaline earth metal-containing detergents -- e.g., one or more neutral or basic alkali or alkaline earth metal salts of at least one sulphonic acid, and/or at least one carboxylic acid, and/or at least one salicyclic acid, and/or at least one alkylphenol, and/or at least one sulphurised alkylphenol, and/or at least one organic phosphorus acid having at least one carbon-to-phosphorus linkage; and
- c) one or more fuel-soluble metal-deactivators of the chelation type.

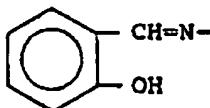
20 The additive compositions are thus composed of three different types of essential or indispensable ingredients, namely, components a), b), and c).

25 In another of its embodiments, this invention provides a fuel composition which comprises a major amount of a liquid hydrocarbonaceous fuel containing a minor combustion-improving amount of components a), b) and c) as just described.

30 Pursuant to preferred embodiments of this invention, the additive

compositions and fuel compositions are essentially halogen-free, that is, they contain no more than 10 ppm of halogen, if any.

Preferred manganese carbonyl compounds - component a) above - are cyclopentadienyl manganese tricarbonyl compounds. The preferred component b) salts are the sodium, potassium, calcium and magnesium salts of sulphonic acids, of alkylphenols, of sulphurised alkylphenols, and of carboxylic acids, especially aromatic carboxylic acids. Preferred metal deactivators for use as component c) are fuel-soluble Schiff bases having one or more chelation centers of the formula



The aromatic ring in the above formula can be further substituted or it can be unsubstituted, and if substituted can contain from 1 to 4 substituents (other than hydrogen atoms), which can be organic or inorganic of any types provided such substituent or plurality of substituents does not interfere with the ability of the metal deactivator to complex with dissolved metals or metal ions and does not otherwise render the metal deactivator unsuitable for use as, for example, by rendering it unstable, pyrophoric, highly toxic, explosive or fuel-insoluble. In other words, any such substituent(s) on the ring should be innocuous.

A feature of this invention is the discovery that the metal deactivator can effectively inhibit fuel destabilisation even when present in the fuel in less than equimolar quantity with respect to either the manganese carbonyl compound(s) or the metal detergent(s) present therein. Another feature of this invention is the discovery that the metal deactivator can effectively inhibit fuel destabilisation while in the presence of still other additive components, such as ashless dispersants, amine stabilisers, and demulsifying agents.

Compositions for use in heating gas oils and similar burner fuels preferably contain, in addition to components a), b) and c) above, one or more of the following:

- d) at least one ashless dispersant;
- e) at least one fuel-soluble demulsifying agent; and
- f) at least one aliphatic or cycloaliphatic amine. Compositions for use in

road diesel fuels and similar middle distillate fuels preferably contain, in addition to components a), b) and c) above, component d), namely, at least one ashless dispersant and/or component e), namely, at least one fuel-soluble demulsifying agent.

5       The above and other embodiments and features of this invention will become apparent from the ensuing description and appended claims.

As used herein the term "fuel-soluble" means that the compound or component under discussion has sufficient solubility at ordinary ambient temperature in the hydrocarbonaceous fuel in which it is to be used to provide a homogeneous solution containing the compound or component in at least the lowest concentration of the concentration ranges specified herein for such compound or component.

10       Manganese carbonyl compounds. The manganese compounds -- component a) -- of the compositions of this invention are characterised by being fuel soluble and by having at least one carbonyl group bonded to a manganese atom.

15       The most desirable general type of manganese carbonyl compounds utilised in accordance with this invention comprise organomanganese polycarbonyl compounds. For best results, use should be made of a cyclopentadienyl manganese tricarbonyl compound of the type described in U. S. Pat. Nos. 2,818,417 and 3,127,351. Thus use can be made of such compounds as cyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl manganese tricarbonyl, ethylcyclopentadienyl manganese tricarbonyl, dimethylcyclopentadienyl manganese tricarbonyl, trimethylcyclopentadienyl manganese tricarbonyl, propylcyclopentadienyl manganese tricarbonyl, isopropylcyclopentadienyl manganese tricarbonyl, butylcyclopentadienyl manganese tricarbonyl, pentylcyclopentadienyl manganese tricarbonyl, hexylcyclopentadienyl manganese tricarbonyl, ethylmethylcyclopentadienyl manganese tricarbonyl, dimethyloctylcyclopentadienyl manganese tricarbonyl, dodecylcyclopentadienyl manganese tricarbonyl, indenyl manganese tricarbonyl, and like compounds in which the cyclopentadienyl moiety contains up to about 18 carbon atoms.

25       A preferred organomanganese compound is cyclopentadienyl manganese tricarbonyl. Particularly preferred for use in the practise of this invention is methylcyclopentadienyl manganese tricarbonyl.

Methods for the synthesis of cyclopentadienyl manganese tricarbonyls are well documented in the literature. See for example, in addition to U. S. Pat. Nos. 2,818,417 and 3,127,351 noted above, U. S. Pat. Nos. 2,868,816; 2,898,354; 2,960,514; and 2,987,529, among others.

5 Other less preferable organomanganese compounds which may be employed include the non-ionic diamine manganese tricarbonyl halide compounds such as bromo manganese dianiline tricarbonyl and bromo manganese dipyridine tricarbonyl, described in U. S. Pat. No. 2,902,489; the acyl manganese tricarbonyls such as methylacetyl cyclopentadienyl manganese tricarbonyl and benzoyl methyl cyclopentadienyl manganese tricarbonyl, described in U. S. Pat. No. 2,959,604; the aryl manganese pentacarbonyls such as phenyl manganese pentacarbonyl, described in U. S. Pat. No. 3,007,953; and the aromatic cyanomanganese dicarbonyls such as mesitylene cyanomanganese dicarbonyl, described in U. S. Pat. No. 3,042,693. Likewise, use can be made of cyclopentadienyl manganese dicarbonyl compounds of  
10 the formula  $RMn(CO)_2L$ , where R is a substituted or unsubstituted cyclopentadienyl group having 5 to 18 carbon atoms, and L is a ligand, such as an olefin, an amine, a phosphine,  $SO_2$ , tetrahydrofuran, or the like. Such compounds are referred to, for example in, Herberhold, M., Metal  $\pi$ -Complexes, Vol. II, Amsterdam, Elsevier, 1967 or Giordano, P. J. and Weighton, M.S., Inorg. Chem., 1977, 16, 160. Manganese  
15 pentacarbonyl dimer (dimanganese decarbonyl) can also be employed if desired.  
20

Metal-containing detergents. The metal-containing detergents are exemplified by oil-soluble neutral and basic salts of alkali or alkaline earth metals with one or more of the following acidic substances (or mixtures thereof): (1) sulphonic acids, (2) carboxylic acids, (3) salicylic acids, (4) alkylphenols, (5) sulphurised alkylphenols,  
25 (6) organic phosphorus acids characterised by at least one direct carbon-to-phosphorus linkage. Such organic phosphorus acids include those prepared by the treatment of an olefin polymer (e.g., polyisobutene having a molecular weight of 1000) with a phosphorising agent such as phosphorus trichloride, phosphorus hepta-sulfide, phosphorus pentasulphide, phosphorus trichloride and sulphur, white phosphorus and a sulphur halide, or phosphorothioic chloride. The most commonly used salts of such acids are those of sodium, potassium, lithium, calcium, magnesium,  
30

strontium and barium.

The term "basic salt" is used to designate metal salts wherein the metal is present in stoichiometrically larger amounts than the organic acid radical. The commonly employed methods for preparing the basic salts involve heating a mineral oil solution of an acid with a stoichiometric excess of a metal neutralising agent such as the metal oxide, hydroxide, carbonate, bicarbonate, or sulphide at a temperature of about 50°C, and filtering the resulting mass. The use of a "promoter" in the neutralisation step to aid the incorporation of a large excess of metal likewise is known. Examples of compounds useful as the promoter include phenolic substances such as phenol, naphthol, alkylphenol, thiophenol, sulphurised alkylphenol, and condensation products of formaldehyde with a phenolic substance; alcohols such as methanol, 2-propanol, octyl alcohol, cellosolve, carbitol, ethylene glycol, stearyl alcohol, and cyclohexyl alcohol; and amines such as aniline, phenylenediamine, phenothiazine, phenyl-betanaphthylamine, and dodecylamine. A particularly effective method for preparing the basic salts comprises mixing an acid with an excess of a basic alkaline earth metal neutralising agent and at least one alcohol promoter, and carbonating the mixture at an elevated temperature such as 60°-200°C.

Examples of suitable metal-containing detergents include, but are not limited to, such substances as lithium phenates, sodium phenates, potassium phenates, calcium phenates, magnesium phenates, sulphurised lithium phenates, sulphurised sodium phenates, sulphurised potassium phenates, sulphurised calcium phenates, and sulphurised magnesium phenates wherein each aromatic group has one or more aliphatic groups to impart hydrocarbon solubility; the basic salts of any of the foregoing phenols or sulphurised phenols (often referred to as "overbased" phenates or "overbased sulphurised phenates"); lithium sulphonates, sodium sulphonates, potassium sulphonates, calcium sulphonates, and magnesium sulphonates wherein each sulphonic acid moiety is attached to an aromatic nucleus which in turn usually contains one or more aliphatic substituents to impart hydrocarbon solubility; the basic salts of any of the foregoing sulphonates (often referred to as "overbased sulphonates"; lithium salicylates, sodium salicylates, potassium salicylates, calcium salicylates, and magnesium salicylates wherein the aromatic moiety is usually

substituted by one or more aliphatic substituents to impart hydrocarbon solubility; the basic salts of any of the foregoing salicylates (often referred to as "overbased salicylates"); the lithium, sodium, potassium, calcium and magnesium salts of hydrolysed phosphosulphurised olefins having 10 to 2000 carbon atoms or of hydrolysed phosphosulphurised alcohols and/or aliphatic-substituted phenolic compounds having 10 to 2000 carbon atoms; lithium, sodium, potassium, calcium and magnesium salts of aliphatic carboxylic acids and aliphatic-substituted cycloaliphatic carboxylic acids; the basic salts of the foregoing carboxylic acids (often referred to as "overbased carboxylates" and many other similar alkali and alkaline earth metal salts of oil-soluble organic acids. Mixtures of salts of two or more different alkali and/or alkaline earth metals can be used. Likewise, salts of mixtures of two or more different acids or two or more different types of acids (e.g., one or more calcium phenates with one or more calcium sulphonates) can also be used. While rubidium, cesium and strontium salts are feasible, their expense renders them impractical for most uses. Likewise, while barium salts are effective, the status of barium as a heavy metal under a toxicological cloud renders barium salts less preferred for present-day usage.

Metal deactivators. As noted above, component c) -- the third indispensable component of the compositions of this invention -- is a metal deactivator of the chelator type, i.e., one or more substances which have the capability of reacting or complexing with dissolved metal and/or metal ions. Examples of the chelator type of metal deactivators include 8-hydroxyquinoline, ethylene diamine tetracarboxylic acid,  $\beta$ -diketones such as acetylacetone,  $\beta$ -ketoesters such as octyl acetoacetate, and the like. The preferred metal deactivators generally regarded as chelators, are Schiff bases, such as N,N'-disalicylidene-1,2-ethanediamine, N,N'-disalicylidene-1,2-propane-diamine, N,N'-disalicylidene-1,3-propanediamine, N,N'-disalicylidene-1,2-cyclohexanediamine, N,N'-disalicylidene-N'-methyl-dipropylenetriamine, 3'-ethoxy-5,2',6'-trimethyl-N,N'-disalicylidene-biphenyl-2,4'-diyldiamine, 5'-ethoxy-3,5,2'-trimethyl-N,N'-disalicylidene-biphenyl-2,4'-diyldiamine, and analogous compounds in which one or more of the salicylidene groups are substituted by innocuous groups such as alkyl, alkoxy, alkylthio, alkenyl, cycloalkyl, cycloalkenyl, aryl, alkoxyalkyl, aralkyl, carboxyl,

esterified carboxyl, etc. Thus a wide variety of known metal deactivators are available for use as component c) in the practise of this invention. The most preferred metal deactivators of this type are N,N'-disalicylidene-1,2-alkanediamines and N,N'-disalicylidene-1,2-cycloalkanediamines, especially N,N'-disalicylidene-1,2-propanediamine. Mixtures of metal deactivators can be used.

We now turn our attention to optional, but preferred, additional components d), e) and f) which may be utilised in the compositions of this invention. As noted above, these additional components do not materially interfere with the enhanced fuel stability realised by combining component c) with components a) and b). Thereafter, other aspects of the invention are considered.

Ashless dispersants. Ashless dispersants, which make up component d), are described in numerous patent specifications, mainly as additives for use in lubricant compositions, but their use in hydrocarbon fuels has also been described. Ashless dispersants leave little or no metal-containing residue on combustion. They generally contain only carbon, hydrogen, oxygen and in most cases nitrogen, but sometimes contain in addition other non-metallic elements such as phosphorus, sulphur or boron.

The preferred ashless dispersant is an alkenyl succinimide of an amine having at least one primary amino group capable of forming an imide group. Representative examples are given in U.S. Pat. Nos. 3,172,892; 3,202,678; 3,216,936; 3,219,666; 3,254,025; 3,272,746; and 4,234,435. The alkenyl succinimides may be formed by conventional methods such as by heating an alkenyl succinic anhydride, acid, acid-ester, acid halide, or lower alkyl ester with an amine containing at least one primary amino group. The alkenyl succinic anhydride may be made readily by heating a mixture of olefin and maleic anhydride to about 180°-220°C. The olefin is preferably a polymer or copolymer of a lower monoolefin such as ethylene, propylene, isobutene and the like. The more preferred source of alkenyl group is from polyisobutene having a molecular weight up to 10,000 or higher. In a still more preferred embodiment the alkenyl group is a polyisobutene group having a molecular weight of about 500-5,000, preferably about 900-2,000, and especially about 900-1,200.

Amines which may be employed in forming the ashless dispersant include any

that have at least one primary amino group which can react to form an imide group. A few representative examples are: methylamine, 2-ethylhexylamine, n-dodecylamine, stearylamine, N,N-dimethyl-propanediamine, N-(3-aminopropyl)morpholine, N-dodecyl-propanediamine, N-aminopropyl-piperazine, ethanolamine, N-ethanol-5 ethylenediamine and the like.

The preferred amines are the alkylene polyamines such as propylene diamine, dipropylene triamine, di-(1,2-butylene)triamine, and tetra-(1,2-propylene)pentamine.

The most preferred amines are the ethylene polyamines which can be depicted by the formula



wherein n is an integer from one to about ten. These include: ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, and the like, including mixtures thereof in which case n is the average value of the mixture. These ethylene polyamines have a primary amine group at each end so can form mono-alkenylsuccinimides and bis-alkenylsuccinimides. Commercially available ethylene polyamine mixtures usually contain minor amounts of branched species and cyclic species such as N-aminoethyl piperazine, N,N'-bis-(aminoethyl)piperazine, N,N'-bis(piperazinyl)ethane, and like compounds. The preferred commercial mixtures have approximate overall compositions falling in the range corresponding to diethylene triamine to tetraethylene pentamine, mixtures generally corresponding in overall makeup to tetraethylene pentamine being most preferred.

Thus especially preferred ashless dispersants for use in the present invention are the products of reaction of a polyethylene polyamine, e.g. triethylene tetramine or tetraethylene pentamine with a hydrocarbon substituted carboxylic acid or anhydride made by reaction of a polyolefin, preferably polyisobutene, having a number average molecular weight of 500 to 5,000, preferably 900 to 2,000 and especially 900 to 1,200, with an unsaturated polycarboxylic acid or anhydride, e.g., maleic anhydride, maleic acid, fumaric acid, or the like, including mixtures of two or 30 more such substances.

Another class of useful ashless dispersants includes alkenyl succinic acid esters

and diesters of alcohols containing 1-20 carbon atoms and 1-6 hydroxyl groups. Representative examples are described in U.S. Pat. Nos. 3,331,776; 3,381,022; and 3,522,179. The alkenyl succinic portion of these esters corresponds to the alkenyl succinic portion of the succinimides described above including the same preferred and most preferred subgenus, e.g., polyisobut enyl succinic acids wherein the polyisobut enyl group has a number average molecular weight of 500 to 5,000, preferably 900-2,000, especially 900 to 1,200.

Alcohols useful in preparing the esters include methanol, ethanol, isobutanol, octadecanol, eicosanol, ethylene glycol, diethylene glycol, tetraethylene glycol, diethylene glycol monoethylether, propylene glycol, tripropylene glycol, glycerol, sorbitol, 1,1,1-trimethylol ethane, 1,1,1-trimethylol propane, 1,1,1-trimethylol butane, pentaerythritol, dipentaerythritol, and the like.

The succinic esters are readily made by merely heating a mixture of alkenyl succinic acid, anhydrides or lower alkyl (e.g., C<sub>1</sub>-C<sub>4</sub>) ester with the alcohol while distilling out water or lower alkanol. In the case of acid-esters less alcohol is used. In fact, acid-esters made from alkenyl succinic anhydrides do not evolve water. In another method the alkenyl succinic acid or anhydrides can be merely reacted with an appropriate alkylene oxide such as ethylene oxide, propylene oxide, and the like, including mixtures thereof.

In another embodiment the ashless dispersant is an alkenyl succinic ester-amide mixture. These may be made by heating the above-described alkenyl succinic acids, anhydrides or lower alkyl esters with an alcohol and an amine either sequentially or in a mixture. The alcohols and amines described above are also useful in this embodiment. Alternatively, amino alcohols can be used alone or with the alcohol and/or amine to form the ester-amide mixtures. The amino alcohol can contain 1-20 carbon atoms, 1-6 hydroxy groups and 1-4 amine nitrogen atoms. Examples are ethanolamine, diethanolamine, N-ethanol-diethylene triamine, and trimethylol aminomethane.

Representative examples of suitable ester-amide mixtures are described in U.S. Pat. Nos. 3,184,474; 3,576,743; 3,632,511; 3,804,763; 3,836,471; 3,862,981; 3,936,480; 3,948,800; 3,950,341; 3,957,854; 3,957,855; 3,991,098; 4,071,548; and

4,173,540.

Such ashless dispersants containing alkenyl succinic residues may, and as is well known, be post-reacted with boron compounds, phosphorus derivatives and/or carboxylic acid acylating agents, e.g. maleic anhydride.

5 Another useful class of ashless dispersants includes the Mannich condensates of hydrocarbyl-substituted phenols, formaldehyde or formaldehyde precursors (e.g. paraformaldehyde) and an amine having at least one primary amine group and containing 1-10 amine groups and 1-20 carbon atoms. Mannich condensates useful in this invention are described in U.S. Pat. Nos. 3,442,808; 3,448,047; 3,539,633; 10 3,591,598; 3,600,372; 3,634,515; 3,697,574; 3,703,536; 3,704,308; 3,725,480; 3,726,882; 3,736,357; 3,751,365; 3,756,953; 3,793,202; 3,798,165; 3,798,247; 3,803,039; and 3,413,347.

15 More preferred Mannich condensates are those made by condensing a polyisobutetyl phenol wherein the polyisobutyl group has an average molecular weight of about 800-3,000 with formaldehyde or a formaldehyde precursor and an ethylene polyamine having the formula:



wherein n is an integer from one to ten or mixtures thereof especially those in which n has an average value of 3-5.

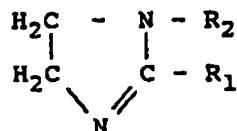
20 Typical post-treated ashless dispersants such as succinimides and Mannich condensates are described in U.S. Pat. Nos. 3,036,003; 3,087,936; 3,200,107; 3,216,936; 3,254,025; 3,256,185; 3,278,550; 3,280,234; 3,281,428; 3,282,955; 3,312,619; 3,366,569; 3,367,943; 3,373,111; 3,403,102; 3,442,808; 3,455,831; 3,455,832; 3,493,520; 3,502,677; 3,513,093; 3,533,945; 3,539,633; 3,573,010; 3,579,450; 3,591,598; 3,600,372; 3,639,242; 25 3,649,229; 3,649,659; 3,658,846; 3,697,574; 3,702,575; 3,703,536; 3,704,308; 3,708,422; and 4,857,214.

A further type of ashless dispersants which can be used comprises inter-polymers of oil-solubilising monomers such as decyl methacrylate, vinyl decyl ether and high molecular weight olefins with monomers containing polar substituents, e.g., 30 aminoalkyl acrylates or acrylamides and poly(oxyethylene)-substituted acrylates. These may be characterised as "polymeric dispersants" and examples thereof are

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disclosed in the following U.S. Pat. Nos.: 3,329,658; 3,449,250; 3,519,565; 565; 3,666,730; 3,687,849; and 3,702,300.

Another class of ashless dispersants which can advantageously be used in the fuel compositions of this invention are the imidazoline dispersants which can be represented by the formula:



wherein R<sub>1</sub> represents a hydrocarbon group having 1 to 30 carbon atoms, e.g. an alkyl or alkenyl group having 7 to 22 carbon atoms, and R<sub>2</sub> represents a hydrogen atoms or a hydrocarbon radical of 1 to 22 carbon atoms, or an aminoalkyl, acylaminoalkyl or hydroxyalkyl radical having 2 to 50 carbon atoms. Such long-chain alkyl (or long-chain alkenyl) imidazoline compounds may be made by reaction of a corresponding long-chain fatty acid (of formula R<sub>1</sub>-COOH), for example oleic acid, with an appropriate polyamine. The imidazoline formed is then ordinarily called, for example, oleylimidazoline where the radical R<sub>1</sub> represents the oleyl residue of oleic acid. Other suitable alkyl substituents in the 2- position of these imidazolines include undecyl, heptadecyl, lauryl and erucyl. Suitable N-substituents of the imidazolines (i.e. radicals R<sub>2</sub>) include hydrocarbyl groups, hydroxyalkyl groups, aminoalkyl groups, and acylaminoalkyl groups. Examples of these various groups include methyl, butyl, decyl, cyclohexyl, phenyl, benzyl, tolyl, hydroxyethyl, aminoethyl, oleylaminoethyl and stearylarninoethyl.

Other suitable ashless dispersants which may be incorporated in the fuel compositions of this invention include the products of condensation of a cyclic anhydride with a straight-chain N-alkyipolyamine of the formula:



where n is an integer at least equal to 1, usually 3 to 5, R is a saturated or unsaturated linear hydrocarbon radical of 10 to 22 carbon atoms and R' is a divalent alkylene or alkylidene radical of 1 to 6 carbon atoms. Examples of such polyamines include N-oleyl-1,3-propanediamine, N-stearyl-1,3-propanediamine, N-oleyl-1,3-

butanediamine, N-oleyl-2-methyl-1,3-propanediamine, N-oleyl-1,3-pentanediamine, N-oleyl-2-ethyl-1,3-propanediamine, N-stearyl-1,3-butanediamine, N-stearyl-2-methyl-1,3-propanediamine, N-stearyl-1,3-pentanediamine, N-stearyl-2-ethyl-1,3-propanediamine, N-oleyl-dipropylenetriamine and N-stearyldipropylenetriamine. Such linear

5 N-alkylpolyamines are condensed with, e.g., a succinic, maleic, phthalic or hexahydrophthalic acid anhydride which may be substituted by one or more radicals of up to 5 carbon atoms each.

Another class of ashless dispersant which can be incorporated in the compositions of the present invention are the products of reaction of an ethoxylated 10 amine made by reaction of ammonia with ethylene oxide with a carboxylic acid of 8 to 30 carbon atoms. The ethoxylated amine may be, for example, mono-, di- or triethanolamine or a polyethoxylated derivative thereof, and the carboxylic acid may be, for example, a straight or branched chain fatty acid of 10 to 22 carbon atoms, a naphthenic acid, a resinic acid or an alkyl aryl carboxylic acid.

15 Still another type of ashless dispersants which can be used in the practise of this invention are the  $\alpha$ -olefin-maleimide copolymers such as are described in U.S. Pat. No. 3,909,215. Such copolymers are alternating copolymers of N-substituted maleimides and aliphatic  $\alpha$ -olefins of from 8 to 30 carbon atoms. The copolymers may have an average of 4 to 20 maleimide groups per molecule. The substituents 20 on the nitrogen of the maleimide may be the same or different and are organic radicals composed essentially of carbon, hydrogen and nitrogen having a total of 3 to 60 carbon atoms. A commercially available material which is highly suitable for use in this invention is <sup>\*</sup>Chevron OFA 425B, and this material is believed to be or comprise an  $\alpha$ -olefin maleimide copolymer of the type described in U.S. Pat. No. 25 3,909,215. Whatever its composition, it works quite well.

All the aforesaid types of ashless dispersants are described in the literature and many are available commercially. Mixtures of various types of ashless dispersants can, of course, be used.

Because of environmental concerns it is desirable to employ ashless 30 dispersants which contain little, if any, halogen atoms such as chlorine atoms. Thus, in order to satisfy such concerns, it is desirable (although not necessary from a

\*Trade-mark

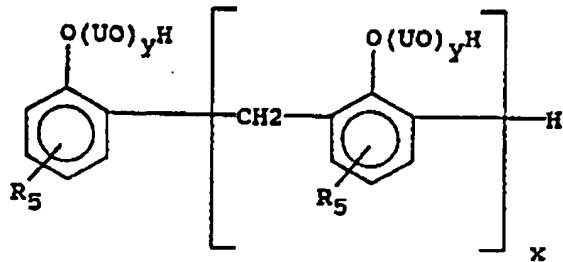
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5 performance standpoint) to select ashless dispersants (as well as the other components used in the compositions of this invention) such that the total halogen content of the overall fuel composition does not exceed 10 ppm. Indeed, the lower the better. Most desirably, the additive composition contains no detectable amount of halogen.

10 Typical halogen (chlorine)-free ashless dispersants suitable for use in the compositions of this invention include, in addition to various types described hereinabove, those described in the following recently-published applications: WO 9003359 and EP 365288.

15 Demulsifying agents. Any of a variety of demulsifying agents can be used in the fuel and fuel additive compositions of this invention. The demulsifying agent improves the water tolerance level of the fuel compositions by minimizing or preventing excessive emulsion formation.

Exemplary demulsifiers which may be employed include poly(alkylphenol) formaldehyde condensates and the polyalkyleneoxy modified reaction products thereof. These compounds are prepared by reacting an alkylphenol with formaldehyde and thereafter reacting the reaction product of the above with a C<sub>2</sub> to C<sub>6</sub> alkylene oxide such as ethylene oxide and propylene oxide. The demulsifiers have a generalized structural formula



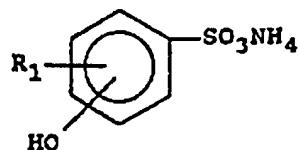
20 wherein U is an alkylene of 2 to 6 carbons; y is an integer averaging between 4 and 10; x is an integer averaging between 4 and 10; and R<sub>5</sub> is an alkyl having from 4 to 15 carbon atoms.

Preferred demulsifiers described by the above formula are polyethylenoxy modified methylene bridged poly(alkylphenol) polymers having a polyethylenoxy

chain of 8 to 20 carbons and preferably from 10 to 16 carbons and at least about 75 number percent of the polyethyleneoxy chains being within the range specified. The methylene bridged poly(alkylphenol) portion of the polymer has from 4 to 10 and preferably from 5 to 8 repeating methylene bridged alkylphenol units with 4 to 15 and preferably 6 to 12 carbons in the alkyl group. In preferred embodiments, the alkyl groups are a mixture of alkyls having between 4 and 12 carbon atoms.

5 Illustrative alkylphenols include p-isobutylphenol, p-diisobutylphenol, p-hexylphenol, p-heptylphenol, p-octylphenol, p-tripropylenepheno1, and p-dipropylenepheno1, etc.

10 Another type of demulsifier component is an ammonia-neutralised sulphonated alkylphenol. These compounds have the general structure:



wherein R<sub>1</sub> is a hydrocarbyl group having from 4 to 15 carbon atoms, preferably from 6 to 12.

15 These compounds are prepared by sulphonating an alkylated phenol and thereafter neutralising the sulphonated product with ammonia.

Another type of demulsifier is an oxyalkylated glycol. These compounds are prepared by reacting a polyhydroxy alcohol such as ethylene glycol, trimethylene glycol, etc., with ethylene or propylene oxide. Many of the compounds are commercially available from BASF-Wyandotte Chemical Company under the PLURONIC trademark. They are polyethers terminated by hydroxy groups and produced by the block copolymerisation of ethylene oxide and propylene oxide. The ethylene oxide blocks act as the hydrophiles and the propylene oxide blocks as the hydrophobes. They are available in a wide range of molecular weights and with varying ratios of ethylene oxide to propylene oxide.

25 One type of commercially available demulsifiers comprises a mixture of alkylarylsulphonates, polyoxalkylene glycols and oxyalkylated alkylphenolic resins.

Such products are supplied by Petrolite Corporation under the TOLAD trademark. One such propriety product, identified as TOLAD 286K, is understood to be a mixture of these components dissolved in a solvent composed of alkyl benzenes. This product has been found efficacious for use in the compositions of this invention. A 5 related product, TOLAD 286, is also suitable. In this case the product apparently contains the same kind of active ingredients dissolved in a solvent composed of heavy aromatic naphtha and isopropanol. However, other known demulsifiers can be used.

10        Aliphatic or cycloaliphatic amine. When it is desired to include one or more amines in the compositions of this invention, any of a wide variety of suitable amines can be used. This component contributes stability to the systems in which it is employed. Typically a monoamine is employed although polyamines can be used, if desired. Among the vast array of suitable amines are included the amines referred 15 to in U.S. Pat. No. 3,909,215 such as tertiary alkyl primary amines including Primene<sup>\*</sup> 81R and the like, and amines referred to in EP 188,042, namely alkyldimethylamines in which the alkyl group has 8 to 14 carbon atoms or mixtures thereof. Also suitable 20 are mixed alkyl-cycloalkyl amines such as N-cyclohexyl-N-butyl amine, N-methyl-cyclohexyl-N-octyl amine, etc., as well as di- and tricycloalkyl amines such as N,N-dicyclohexyl amine, N,N-di-(ethylcyclohexyl)amine, N,N,N-tricyclohexyl amine, and the like. Preferred amines include N-cycloalkyl-N,N-dialkyl amines and 25 N-cycloalkenyl-N,N-dialkylamines such as N-cyclohexyl-N,N-diethyl amine, N-cyclohexyl-N,N-dibutyl amine, N-cycloheptyl-N,N-dimethyl amine, N-cyclooctyl-N,N-dilauryl amine, N-cyclohexenyl-N,N-dipropyl amine, and like compounds. Particularly preferred is N-cyclohexyl-N,N-dimethyl amine. Mixtures of various amines, such as those referred to above, are also suitable for use in accordance with this invention.

25        Hydrocarbonaceous fuels. In principle, the advantages of this invention may be achieved in any liquid hydrocarbonaceous fuel derived from petroleum, coal, shale and/or tar sands. In most instances, at least under present circumstances, the base fuels will be derived primarily, if not exclusively, from petroleum.

30        The invention is thus applicable to such fuels as kerosene, jet fuel, aviation fuel, diesel fuel, home heating oil, light cycle oil, heavy cycle oil, light gas oil, heavy gas oil, bunker fuels, residual fuel oils, ultra heavy fuel oils, and in general, any liquid

\*Trade-mark

(or flowable) hydrocarbonaceous product suitable for combustion either in an engine (e.g., diesel fuel, gas turbine fuels, etc.) or in a burner apparatus (e.g., gas oils, inland heavy fuel oil, residual fuel oils, visbreaker fuel oils, home heating oils, etc.). Other suitable fuels may include liquid fuels derived from biomass, such as vegetable oils (e.g., rapeseed oil, jojoba oil, cottonseed oil, etc.); or refuse-derived liquid fuels such as fuels derived from municipal and/or industrial wastes; or waste oils and/or liquid waste biomass and its derivatives; or mixtures of any of the foregoing substances.

In many cases, specifications exist for various hydrocarbonaceous fuels or grades thereof, and in any event the nature and character of such fuels are well-known and reported in the literature.

The additive compositions comprising components a), b), c) and at least one of components d), e) and f) – preferably two of components d), e) and f) and most preferably all three of components d), e) and f) – are especially useful in heating gas oils and like burner fuels and fuel oils for agricultural and industrial engines. Typical specifications for such fuel oils can be found, for example, in BS 2869 : Part 2 : 1988 of the British Standards Institution. Typical specifications for automotive or road diesel fuels, in which compositions composed of components a), b), c), d) and e) are especially useful, appear in BS 2869: Part 1: 1988 of the British Standards Institution. As can be appreciated, a vast number of such specifications exist from country to country.

Concentrations and proportions. In general, the components of the additive compositions, especially components a) and b), are employed in the fuels in minor amounts sufficient to improve the combustion characteristics and properties of the base hydrocarbonaceous fuel in which they are employed. The metal deactivator, component c), is employed in a minor amount sufficient to inhibit fuel destabilisation in fuels containing components a) and b). The amounts will thus vary in accordance with such factors as base fuel type and service conditions for which the finished fuel is intended. However, generally speaking, the following concentrations (ppm) of the components (active ingredients) in the base fuels are illustrative:

	<u>General Range</u>	<u>Preferred Range</u>	<u>More Preferred Range</u>	<u>Particularly Preferred Range</u>	
	Component a)	1.5-10,000	2.5-1,500	3-100	3-25
5	Component b)	4-10,000	5-6,000	6-300	6-100
	Component c)	0.1-6,000	0.25-1,000	1-500	1.5-100

In the case of fuels additionally containing one or more of components d), e), and f), the following concentrations (ppm) of active ingredients are typical:

	<u>General Range</u>	<u>Preferred Range</u>	<u>Particularly Preferred Range</u>	
10	Component d)	0-15,000	8-5,000	10-200
	Component e)	0-4,000	0.5-200	2-50
	Component f)	0-10,000	5-200	10-50

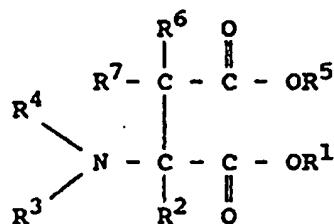
15 It will be appreciated that the individual components a), b), and c), and also d), e), and/or f) (if used), can be separately blended into the fuel or can be blended therein in various subcombinations, if desired. Ordinarily, the particular sequence of such blending steps is not critical. Moreover, such components can be blended in the form of a solution in a diluent. It is preferable, however, to blend the components used in the form of an additive concentrate of this invention, as this simplifies the blending operations, reduces the likelihood of blending errors, and takes advantage of the compatibility and solubility characteristics afforded by the overall concentrate.

20 The additive concentrates of this invention will contain components a), b), and c), and optionally, but preferably, one or more of components d), e), and f) in amounts proportioned to yield fuel blends consistent with the concentrations tabulated above. In most cases, the additive concentrate will contain one or more diluents such as light mineral oils, to facilitate handling and blending of the

concentrate. Thus concentrates containing up to 90% by weight of one or more diluents or solvents are frequently used.

Other components. If desired or deemed of help in given situations, one or more other components can be included in the compositions of this invention. For example, the additive compositions and fuel compositions of this invention can also contain antioxidant, e.g., one or more phenolic antioxidants, aromatic amine antioxidants, sulphurised phenolic antioxidants, and organic phosphites, among others. Examples include 2,6-di-tert-butylphenol, liquid mixtures of tertiary butylated phenols, 2,6-di-tert-butyl-4-methylphenol, 4,4'-methylenebis(2,6-di-tert-butylphenol), 2,2'-methylenebis(4-methyl-6-tert-butylphenol), mixed methylene-bridged polyalkyl phenols, 4,4'-thiobis(2-methyl-6-tert-butylphenol), N,N'-di-sec-butyl-p-phenylenediamine, 4-isopropylaminodiphenyl amine, phenyl- $\alpha$ -naphthyl amine, and phenyl- $\beta$ -naphthyl amine.

Corrosion inhibitors comprise another type of optional additive for use in this invention. Thus use can be made of dimer and trimer acids, such as are produced from tall oil fatty acids, oleic acid, linoleic acid, or the like. Products of this type are currently available from various commercial sources, such as, for example, the dimer and trimer acids sold under the HYSTRENE trademark by the Humco Chemical Division of Witco Chemical Corporation and under the EMPOL trademark by Emery Chemicals. Another useful type of corrosion inhibitor for use in the practise of this invention are the alkenyl succinic acid and alkenyl succinic anhydride corrosion inhibitors such as, for example, tetrapropenylsuccinic acid, tetrapropenylsuccinic anhydride, tetradecenylsuccinic acid, tetradecenylsuccinic anhydride, hexadecenylsuccinic acid, hexadecenylsuccinic anhydride, and the like. Also useful are the half esters of alkenyl succinic acids having 8 to 24 carbon atoms in the alkenyl group with alcohols such as the polyglycols. Preferred materials are the aminosuccinic acids or derivatives thereof represented by the formula:



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wherein each of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and R<sup>7</sup> is, independently,  
a hydrogen atom or a hydrocarbyl group containing 1 to 30 carbon atoms, and  
wherein each of R<sup>3</sup> and R<sup>4</sup> is, independently, a hydrogen atom, a hydrocarbyl group  
containing 1 to 30 carbon atoms, or an acyl group containing from 1 to 30 carbon  
5 atoms.

The groups R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup>, when in the form of a hydrocarbyl  
group, can be, for example, alkyi, cycloalkyl or aromatic containing groups. Preferably R<sup>1</sup> and R<sup>5</sup> are the same or different straight-chain or branched-chain  
10 hydrocarbon radicals containing 1-20 carbon atoms. Most preferably, R<sup>1</sup> and R<sup>5</sup> are  
saturated hydrocarbon radicals containing 3-6 carbon atoms. R<sup>2</sup>, either R<sup>3</sup> or R<sup>4</sup>, R<sup>6</sup>  
and R<sup>7</sup>, when in the form of hydrocarbyl groups, are preferably the same or different  
15 straight-chain or branched-chain saturated hydrocarbon radicals. Preferably a dialkyl  
ester of an aminosuccinic acid is used in which R<sup>1</sup> and R<sup>5</sup> are the same or different  
alkyl groups containing 3-6 carbon atoms, R<sup>2</sup> is a hydrogen atom, and either R<sup>3</sup> or  
R<sup>4</sup> is an alkyl group containing 15-20 carbon atoms or an acyl group which is derived  
from a saturated or unsaturated carboxylic acid containing 2-10 carbon atoms.

Most preferred is a dialkylester of an aminosuccinic acid of the above formula  
wherein R<sup>1</sup> and R<sup>5</sup> are isobutyl, R<sup>2</sup> is a hydrogen atom, R<sup>3</sup> is octadecyl and/or  
octadecenyl and R<sup>4</sup> is 3-carboxy-1-oxo-2-propenyl. In such ester R<sup>6</sup> and R<sup>7</sup> are most  
20 preferably hydrogen atoms.

The heavier fuels of this invention may contain cold flow improvers and  
pour-point depressants, e.g., olefin/vinyl acetate copolymers such as ethylene/vinyl  
acetate copolymers and polymethacrylates. Antifoam agents such as silicones; metal  
deactivators of the passivator type, e.g., the thiadiazoles such as HITEC® 314  
25 additive (Ethyl Petroleum Additives, Ltd.; Ethyl Petroleum Additives, Inc.); and dyes  
can also be used in the compositions of this invention. The diesel fuels may contain  
cetane improvers such as peroxy compounds and organic nitrates (e.g., amyl nitrates,  
hexyl nitrates, heptyl nitrates, octyl nitrates, and other alkyl nitrates having about 4  
to about 10 carbon atoms including mixtures thereof). A few specific examples of  
30 such alkyl nitrates are cyclohexyl nitrate, methoxypropyl nitrate, mixed nitrate esters  
made by nitration of fusel oil, 2-ethylhexyl nitrate, n-octyl nitrate, n-decyl nitrate, etc.

Typical peroxy compounds include acetyl peroxide, benzoyl peroxide, tert-butyl-peroxyacetate, and cumene hydroperoxide.

5 All of the foregoing optional other components are well known in the art and are used in the usual proportions. In selecting such optional component(s), care should be taken to ensure that the selected material or combination of material is compatible with components of the overall composition in which it is being used.

The following non-limiting examples in which all parts and percentages are by weight illustrate the invention.

EXAMPLE 1

10 An additive composition is formed by blending together the following components in the amounts specified:

4.0% Methylcyclopentadienyl manganese tricarbonyl (MMT) as a blend containing 62% MMT and 38% diluent (mainly aromatic solvent);

15 6.0% Overbased calcium sulphonate as a blend with 44% 100 solvent neutral oil and having a typical TBN of 295;

1.6% N,N'-disalicylidene-1,2-propanediamine as an 80% solution in xylene; and 88.4% Heavy aromatic naphtha.

This composition is well adapted for use in heating gas oil, for example at treat rates of 250 to 37,000 ppm, typically 500 ppm.

EXAMPLE 2

20 An additive composition is formed by blending together the following components in the amounts specified:

4.0% Methylcyclopentadienyl manganese tricarbonyl (MMT) as a blend containing 62% MMT and 38% diluent (mainly aromatic solvent);

25 6.0% Overbased calcium sulphonate as a blend with 44% 100 solvent neutral oil and having a typical TBN of 295;

1.2% N,N'-disalicylidene-1,2-propanediamine as an 80% solution in xylene; and 88.8% Heavy aromatic naphtha.

30 This composition is well adapted for use in heating gas oil, for example at treat rates of 250 to 37,000 ppm, typically 500 ppm.

EXAMPLE 3

An additive composition is formed by blending together the following components in the amounts specified:

- 4.0% Methylcyclopentadienyl manganese tricarbonyl (MMT) as a blend containing  
5        62% MMT and 38% diluent (mainly aromatic solvent);  
6.0% Overbased calcium sulphonate as a blend with 44% 100 solvent neutral oil  
and having a typical TBN of 295;  
1.6% N,N'-disalicylidene-1,2-propanediamine as an 80% solution in xylene;  
9.2% Chevron OFA 425B, an ashless dispersant believed to comprise a C<sub>13</sub>/C<sub>16</sub>  
10        α-olefin-maleic anhydride copolymer aminated with an N-alkylpropylene  
            diamine as a 50% solution in oil;  
9.2% N-cyclohexyl-N,N-dimethylamine; and  
70.0% Heavy aromatic naphtha.

This composition is well adapted for use in heating gas oil, for example at  
15        treat rates of 250 to 37,000 ppm, typically 500 ppm.

EXAMPLE 4

An additive composition is formed by blending together the following components in the amounts specified:

- 4.0% Methylcyclopentadienyl manganese tricarbonyl (MMT) as a blend containing  
20        62% MMT and 38% diluent (mainly aromatic solvent);  
6.0% Overbased calcium sulphonate as a blend with 44% 100 solvent neutral oil  
and having a typical TBN of 295;  
1.6% N,N'-disalicylidene-1,2-propanediamine as an 80% solution in xylene;  
6.9% Chevron OFA 425B, an ashless dispersant believed to comprise a C<sub>13</sub>/C<sub>16</sub>  
25        α-olefin-maleic anhydride copolymer aminated with an N-alkylpropylene  
            diamine as a 50% solution in oil;  
5.2% N-cyclohexyl-N,N-dimethylamine; and  
76.3% Heavy aromatic naphtha.

This composition is well adapted for use in heating gas oil, for example at  
30        treat rates of 250 to 37,000 ppm, typically 500 ppm.

EXAMPLE 5

The procedure of Example 3 is repeated using the following proportions of the additive components:

- 4.0% MMT as the blend of Example 3;  
5 6.0% Overbased calcium sulphonate as the blend of Example 3;  
1.2% N,N'-disalicylidene-1,2-propanediamine as the solution of Example 3;  
6.9% Chevron OFA 425B, as the solution of Example 3;  
6.9% N-cyclohexyl-N,N-dimethylamine; and  
75.0% Heavy aromatic naphtha.

10 EXAMPLE 6

The procedure of Example 3 is repeated using the following proportions of the additive components:

- 4.0% MMT as the blend of Example 3;  
15 6.0% Overbased calcium sulphonate as the blend of Example 3;  
1.2% N,N'-disalicylidene-1,2-propanediamine as the solution of Example 3;  
6.9% Chevron OFA 425B, as the solution of Example 3;  
5.2% N-cyclohexyl-N,N-dimethylamine; and  
76.7% Heavy aromatic naphtha.

20 EXAMPLE 7

- An additive composition of this invention is formed using the following:  
25 4.0% MMT as the 62% solution in diluent specified in Example 1;  
6.0% Overbased calcium sulphonate as the blend in 100 solvent neutral oil specified in Example 1;  
1.6% N,N'-disalicylidene-1,2-propanediamine as an 80% solution in heavy aromatic naphtha;  
30 5.5% Polyisobutylene succinimide of tetraethylene pentamine (made from polybutenes with Mn of approximately 950) as a 25% solution in oil;  
1.4% Akzo Armogard <sup>\*</sup>D5021 demulsifier, believed to be a blend of demulsifier bases and surfactants in an aromatic solvent;  
5.2% N-cyclohexyl-N,N-dimethylamine; and  
76.3% Heavy aromatic naphtha.

\*Trade-mark

This composition is useful, for example at treat rates of 250 to 37,000 ppm, typically 500 ppm, in heating gas oils.

#### EXAMPLE 8

Using the procedure of Example 1, the following components are blended together:

- 5      4.5% MMT blend specified in Example 1;
- 33.0% Overbased calcium sulphonate blend specified in Example 1;
- 1.8% N,N'-disalicylidene-1,2-butanediamine as a 75% solution in heavy aromatic naphtha;
- 10     22.7% Polyisobutetyl succinimide of tetraethylene pentamine (made from polybutene of Mn of approximately 950) as a 23% solution in a solvent oil;
- 6.8% Demulsifier (Tolad 286K); and
- 31.2% Heavy aromatic naphtha diluent.

When used, for example at a concentration in the range of 200 to 26,500 ppm, typically 400 ppm, this additive concentrate is especially adapted for improving combustion of road diesel fuels.

#### EXAMPLE 9

An additive concentrate is formed using the following components:

- 20     2.8% MMT;
- 14.5% Overbased calcium sulphonate blend;
- 1.5% N,N'-disalicylidene-1,2-cyclohexanediamine as a 60% solution in aromatic naphtha;
- 17.1% Polyisobutetyl succinimide of an equivalent mixture of diethylene triamine, triethylene tetramine, and tetraethylene pentamine (made from polyisobutene of Mn of approximately 1000); and
- 25     64.1% Inert diluents (primarily 100 solvent neutral mineral oil).

#### EXAMPLE 10

The following additive concentrate is formed:

- 30     5.0% Cyclopentadienyl manganese tricarbonyl in a blend containing 40% aromatic hydrocarbon solvent;
- 30.5% Overbased magnesium sulphonate;

- 1.8% N,N'-disalicylidene-1,2-propanediamine;  
24.5% Mannich condensation product of p-(polysisobuteny)phenol (made from  
polysisobutene of Mn of 750), formaldehyde and triethylene tetramine;  
5.6% Akzo Armogard D5021 demulsifier; and  
5 32.6% Heavy aromatic naphtha diluents.

EXAMPLE 11

Examples 9 and 10 are repeated substituting in one case overbased potassium sulphonate and in another case overbased calcium phenate for the sulphonates of Examples 9 and 10.

10 EXAMPLE 12

The procedures of Examples 4, 7 and 8 are repeated except that in one case the overbased calcium sulphonate is replaced by an equivalent amount of overbased magnesium sulphonate, in another case by an equivalent amount of overbased sodium sulphonate, and in a third case by an equivalent amount of overbased 15 potassium sulphonate.

EXAMPLE 13

The respective compositions of Examples 1 through 9 and 12 are formed with the exception that the methylcyclopentadienyl manganese tricarbonyl is replaced in one case by an equivalent amount of cyclopentadienyl manganese tricarbonyl, in 20 another case by an equivalent amount of cyclopentadienyl manganese dicarboxyl triphenylphosphine, in a third case by an equivalent amount of indenyl manganese tricarbonyl, in a fourth case by an equivalent amount of dimanganese decacarbonyl, and in still another case by an equivalent amount of a mixture composed of 90% methylcyclopentadienyl manganese tricarbonyl and 10% cyclopentadienyl manganese 25 tricarbonyl.

EXAMPLE 14

The respective compositions of Examples 4 and 7 are blended at concentrations of 300, 500 and 1,000 ppm in a heating gas oil having a specific gravity at 15°C (DIN 51 757) of 0.845 g/mL, a kinematic viscosity at 20°C (DIN 51 562) of 5.3 mm<sup>2</sup> 30 per second, a pour point (DIN ISO 3016) of -9°C, a sulphur content (DIN 51 400) of 0.19%, and a distillation profile (DIN 51 751) of 27 volume % boiling to 250°C

and 92 volume % boiling to 350°C.

EXAMPLE 15

Example 14 is repeated except that the same amounts of the respective components of the respective compositions of Examples 4 and 7 are blended individually or in sub-combinations into the gas oil.

EXAMPLE 16

The composition of Example 8 is blended at concentrations of 300, 500, 1,000 and 1,500 ppm in a diesel fuel satisfying the requirements of DIN 51 601-DK (February 1986).

EXAMPLE 17

Example 16 is repeated except that the same amounts of the respective components of the composition of Example 8 are blended individually or in sub-combinations into the diesel fuel.

EXAMPLE 18

The procedures of Examples 16 and 17 are repeated using commercially available diesel fuels suitable for use as railway diesel fuel, tractor diesel fuel, off-road diesel fuel and inland waterways fuel.

EXAMPLE 19

Examples 14 and 15 are repeated using as the fuels commercially-available heavy fuel oils and residual oils (e.g., industrial and refinery fuel oils) such as inland heavy fuel oils, and also hydrocarbonaceous marine fuels. The additive treat levels in these fuels are 500, 800 and 1,500 ppm.

The enhanced stability characteristics of the compositions of this invention are illustrated by the results of a series of thermal oxidative stability tests conducted in accordance with ASTM Test Procedure D2274. In these tests two different commercially-available base fuels were used. One was a relatively stable diesel fuel having a cetane number of 52.7 (Fuel A). The other was a relatively unstable diesel fuel having a cetane number of 52.5 (Fuel B). Each of these fuels was tested in duplicate without the addition thereto of any additives. In addition Fuels A and B containing various additive mixtures based on the combination of MMT and calcium sulphonate both with and without metal deactivator of the chelation type were subjected to the

same ASTM test procedure. The compositions tested and the results obtained are summarised in the following table in which the additive components were as follows:

- "MMT" as the 62% blend as in Example 1;
  - "Ca Det." is calcium sulphonate as the 44% blend as in Example 1;
  - 5 "Metal Deact." is metal deactivator in the form of the 80% solution of N,N'-disalicylidene-1,2-propanediamine as in Example 1;
  - "Disp." is Chevron OFA 425B ashless dispersant in the form of a 50% solution as in Example 3;
  - 10 "Amine" in the form of N-cyclohexyl-N,N-dimethylamine stabiliser; and
  - "Dil." is diluent in the form of heavy aromatic naphtha.
- All tests involving use of an additive mixture were run at a total additive concentration of 500 ppm in the fuel. In the table "--" signifies "none", the numerical values for the additive components represent the weight percentage of the component in the form listed above, and the results are expressed in terms of milligrams of deposit per 100 milliliters of fuel. Test Nos. 1-6 were performed in Fuel A and Test Nos. 7-13 in Fuel B.
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Thermal Oxidative Stability Tests

<u>Test No.</u>	<u>MMT</u>	<u>Ca Det.</u>	<u>Metal Deact.</u>	<u>Disp.</u>	<u>Amine</u>	<u>Dil.</u>	<u>Deposits, mg/mL</u>
1	--	--	--	--	--	--	0.28
5	2	--	--	--	--	--	0.34
	3	4	6	--	20	70	1.83
	4	4	6	1.2	6.9	5.2	2.88
	5	4	6	1.6	9.2	9.2	0.09
	6	4	6	1.6	6.9	5.2	0.23
10	7	--	--	--	--	--	1.31
	8	--	--	--	--	--	1.86
	9	4	6	--	7.5	6.9	75.6
	10	4	6	1.2	6.9	6.9	0.34
	11	4	6	1.2	6.9	5.2	76.7
15	12	4	6	1.6	9.2	9.4	0.03
	13	4	6	1.6	9.2	9.2	0.06

It will be seen from the results in the above table that in the relatively stable Fuel A the combination of the manganese compound and the calcium-containing detergent (Test No. 3) caused a significant loss in fuel stability as compared to the additive-free fuel (Test Nos. 1 and 2). It will also be noted that this fuel destabilisation occurred notwithstanding the presence in the fuel of a relatively high concentration of N-cyclohexyl-N,N-dimethylamine, a known fuel stabiliser. From Test No. 4 it is seen that in this particular fuel, 1.2% of the metal deactivator blend in the additive mixture (at 500 ppm) was insufficient to combat the fuel destabilisation. On the other hand, Test Nos. 5 and 6 show that 1.6% of the metal deactivator in the additive mixture (at 500 ppm) greatly increased the stability of the fuel composition. Thus in Fuel A there is a threshhold concentration in the systems tested at 500 ppm falling between these 1.2% and 1.6% additive proportions.

In the less stable fuel (Fuel B), it is seen from Test No. 9 that once again the combination of the manganese compound and the calcium-containing detergent

resulted in a further loss of fuel stability as compared to the additive-free fuel (Tests 7 and 8). And from Test Nos. 10 through 13 it is seen that in Fuel B both 1.2% and 1.6% of the metal deactivator in the additive mixtures conferred at the 500 ppm additive mixture level, very substantial improvements in fuel stability. Thus in Fuel 5 B the threshhold concentration in the system at 500 ppm corresponds to less than 1.2% of the metal deactivator in the additive composition.

The effectiveness and advantageous characteristics of the compositions of this invention are illustrated by the results of a number of other standardised tests. For example, an 81 kW gas oil-fired hot water boiler was operated with a flue gas 10 temperature of 207°C, a carbon dioxide flue gas content of 12.1% and a carbon monoxide flue gas content of above 100 ppm. The base heating gas oil was as specified in Example 14. Operation of the boiler on the additive-free gas oil gave a Bacharach soot number of 4.60 whereas the same gas oil containing 500 ppm of the additive composition of Example 4 gave a Bacharach soot number of 2.70, a 41% 15 reduction. Measurements of the acidity of the soot (an average of 4 determinations) showed that the clear base gas oil produced a soot with an average pH of 4.05. In contrast the soot from the fuel of this invention had a pH averaging 7.06.

Standard CFR engine tests (ASTM D613) were conducted using two different diesel fuels having cetane values of 52.7 (Fuel A) and 52.5 (Fuel B), respectively. 20 Addition of 500 ppm of the composition of Example 4 to Fuel A caused no change in cetane rating. In Fuel B only a slight loss in cetane value (from 52.5 to 51.6) occurred by addition of 500 ppm of the composition of Example 4.

The same pair of diesel fuels were subjected to standard corrosion tests (ASTM 665A), both with and without 500 ppm of the additive composition of 25 Example 4. The results of these tests were as follows:

Rating Per ASTM 665A

Fuel A without additives	D, D
Fuel A with additives	A, A
Fuel B without additives	B, B+
30 Fuel B with additive	A, A

Diesel fuels both with and without the additive composition of this invention as set forth in Example 7 were subjected to standard corrosion tests (ASTM 665A) and (ASTM 665B). The results were as follows:

	Rating Per <u>ASTM 665A</u>	Rating Per <u>ASTM 665B</u>
5		
Fuel A without additives	C, C	E, E
Fuel A with additives	A, A	E, E
Fuel B without additives	B+, B+	D, D
Fuel B with additives	A, A	D, D

10 The same compositions were subjected to thermal stability tests wherein the sample is heated at 150°C for 90 minutes, filtered through a filter and the reflectance of the deposit on the filter measured. The rating scale ranges from 0 (clean) to 20 (black). A rating of 7 or less is considered good. Thermal oxidative stability tests according to ASTM D 2274 were also performed on these fuel compositions. The performance in these tests is expressed in terms of milligrams of deposit per 100 milliliters of fuel. The results were as follows:

	Thermal Stability (Filter Tests)	Thermal Oxidative Stability (ASTM D2274)
20		
Fuel A without additives	6	0.15
Fuel A with additives	3	0.17
Fuel B without additives	19	4.45
Fuel B with additives	6	0.14

25 Demulsification tests (ASTM D 1094) on the same four fuels gave the results shown below:

	<u>Interface Rating</u>	<u>Separation Rating</u>	<u>Volume of Aqueous Phase, mL</u>
	Fuel A without additives	4	3
5	Fuel A with additives	3	3
	Fuel B without additives	4	3
	Fuel B with additives	3	19

Additional tests were run using a commercially available domestic heating gas oil in order to determine performance in two different burners. One was a modern burner whereas the other was a burner produced fifteen years ago. In each case the burners were adjusted to the manufacturer's specifications. The additive compositions of Examples 4 and 7 were utilised in these tests together with baseline runs on the clear base fuel. Measurements were made of the smoke number and for carbon monoxide content of the flue gases. The smoke number determinations involve a scale ranging from 0 to 10, which ratings are applied to a filter through which the flue gas was passed during the operation. A rating of 10 means black and thus the lower the number, the better. The carbon monoxide ratings are expressed in terms of parts per million in the flue gas. The following table summarises these data.

		<u>Old Burner</u>		<u>New Burner</u>	
		<u>Smoke No.</u>	<u>CO</u>	<u>Smoke No.</u>	<u>CO</u>
	Base fuel without additives	5.5	80	1	90
	Base fuel with additives <sup>a</sup>	5.5	43	--	--
	Base fuel with additives <sup>b</sup>	4.0	40	0	18
25	Base fuel with additives <sup>c</sup>	4.5	40	0	20
	Base fuel with additives <sup>d</sup>	3.5	45	0	25

- a Additive composition of Example 4 at 500 ppm  
 b Additive composition of Example 4 at 1000 ppm  
 c Additive composition of Example 7 at 500 ppm  
 d Additive composition of Example 7 at 1000 ppm

The above and other test results have indicated that the fuels of this invention generally possess enhanced combustion properties (e.g., less smoke, lower soot acidity) and better thermal stability than the corresponding untreated fuels. In addition, use of the fuels of this invention results in the formation of reduced amounts of sludge deposits on critical engine or burner parts or surfaces. Further, such fuels tend to emit smaller amounts of noxious emissions than the corresponding untreated base fuels. Also this invention enables the provision of fuel compositions having enhanced demulsification properties and reduced corrosion tendencies with minimal interference with other desirable fuel properties. The additive compositions of this invention can result in decreased fuel consumption in diesel engines. The above data indicate that all fuels do not necessarily respond to the same extent to treatment with the additive systems of this invention. Nonetheless, as a general proposition, the fuels of this invention do have significantly improved properties.

It will be seen from the foregoing that this invention includes among its embodiments methods of improving the combustion characteristics and stability of an at least predominantly hydrocarbonaceous liquid fuel which comprises blending therewith a minor combustion-improving amount of:

- a) at least one fuel-soluble manganese carbonyl compound; and
- b) at least one fuel-soluble alkali or alkaline earth metal-containing detergent;

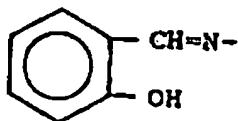
and a minor stabilising amount of:

- c) at least one fuel-soluble metal deactivator of the chelation type.

Such compositions preferably contain one or more of components d), e) and f) as described hereinabove.

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1. A fuel composition which comprises a major amount of a liquid hydrocarbonaceous fuel containing a minor combustion-improving amount of
  - a. 1.5 to 10,000 ppm of a fuel-soluble manganese carbonyl compound;
  - b. 4.0 to 10,000 ppm of a fuel-soluble alkali or alkaline earth metal-containing detergent;
 and a minor stabilising amount of:
  - c. 0.1 to 6,000 ppm of a fuel-soluble metal deactivator of the chelation type which has the capability of reacting or complexing with dissolved metal and/or metal ions;
  - d. 15,000 ppm or less of a fuel-soluble demulsifying agent; and
  - e. 4,000 ppm or less of a fuel-soluble aliphatic or cycloaliphatic amine.
2. A composition according to claim 1 wherein component a) comprises at least one cyclopentadienyl manganese tricarbonyl compound.
3. A composition according to claim 1 or 2 wherein component b) comprises at least one overbased alkali or alkaline earth metal-containing detergent.
4. A composition according to claim 1, 2 or 3 wherein component c) consists essentially of at least one fuel-soluble Schiff base having one or more chelation centers of the formula



wherein the aromatic ring can contain up to 4 innocuous substituents in place of hydrogen atoms.

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5. A composition according to any one of claims 1 to 4 which contains e) at least one fuel-soluble N-cycloalkyl-N,N-dialkylamine.
6. A composition according to any one of claims 1 to 5 which contains 10 ppm or less halogen.
7. A fuel additive composition which comprises ingredients a), b), c), optionally d) and optionally e) as defined in any one of claims 1 to 5.
8. A method of improving the combustion characteristics and stability of a liquid fuel, said liquid fuel containing a major amount of a hydrocarbonaceous liquid fuel, which comprises blending therewith a minor combustion-improving amount of ingredients a), b), c), optionally d) and optionally e) as defined in any one of claims 1 to 5.
9. A composition according to claim 2 wherein said cyclopentadienyl manganese tricarbonyl compound consists essentially of methylcyclopentadienyl manganese tricarbonyl.
10. A composition according to claim 3 wherein said overbased alkali or alkaline earth metal-containing detergent consists essentially of at least one sulphonate detergent.
11. A composition according to claim 10 wherein said sulphonate detergent is an overbased calcium sulphonate detergent.
12. A composition according to claim 4 wherein said aromatic ring which can contain up to 4 innocuous substituents in place of hydrogen atoms is a salidylidene diamine.
13. A composition according to claim 12 wherein said salidylidene diamine is an N,N'-disalicylidene-1,2-alkanediamine or N,N'-disalicylidene-1,2-cycloalkanediamine.

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14. A composition according to claim 13 wherein said N,N'-disalicylidene-1,2-alkanediamine or N,N'-disalicylidene-1,2-cycloalkanediamine is N,N'-disalicylidene-1,2-propanediamine.
15. A composition according to claim 5 wherein said N-cycloalkyl-N,N-dialkylamine is N-cyclohexyl-N,N-dimethylamine.
16. A composition according to any one of claims 1 to 15 wherein the proportions of components a), b) and c) in parts by weight are 2.5-1,500 : 5-6,000 : 0.5-1,000.
17. A composition according to any one of claims 1 to 16 wherein the proportions of components a), b) and c) in parts by weight are 3-100 : 6-300 : 1-500.
18. A composition according to any one of claims 1 to 17 wherein the proportions of components a), b) and c) in parts by weight are 3-25 : 6-100 : 1.5-100.
19. A composition according to any one of claims 1 to 18 which is free of any detectable quantity of contained halogen.